



I, the undersigned, who have prepared English translations which are attached herewith, hereby declare that the aforementioned translations are true and correct translations of officially certified copies of the Korean Patent Application Nos. 2002-46580 and 2003-28968 filed on August 7, 2002, and May 7, 2003, respectively.

This 15th day of December, 2006

Translator:

A handwritten signature in cursive script, appearing to read "Hyo-Jin Kim", written over a horizontal line.

Hyo-Jin Kim



[ABSTRACT OF THE DISCLOSURE]

The present invention relates to a polymer electrolyte for a lithium sulfur battery, and a lithium sulfur battery including the same, and the electrolyte includes a monomer with a methacrylate group, a C₆ to C₄₀ peroxide, and an electrolytic solution including an organic solvent, and a lithium salt.

The polymer electrolyte of the present invention can provide a lithium sulfur battery exhibiting improved cycle life characteristics and safety.

[Representative Drawings]

FIG. 1

[Key words]

Polymer electrolyte, lithium sulfur battery, polyesterpolyol



[SPECIFICATION]

[TITLE OF THE INVENTION]

POLYMER ELECTROLYTE FOR LITHIUM-SULFUR BATTERY AND LITHIUM-SULFUR BATTERY COMPRISING SAME

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a photograph showing a negative electrode according to Example 1 of the present invention, after a cycle life test of the lithium sulfur cell was done;

FIG. 2 is a photograph showing a negative electrode according to Comparative Example 1, after a cycle life test of the lithium sulfur cell was done; and

FIG. 3 is a graph illustrating cycle life characteristics of the lithium sulfur cells according to Example 1 of the present invention and Comparative Example 1.

[DETAILED DESCRIPTION OF THE INVENTION]

[OBJECT OF THE INVENTION]

[FIELD OF THE INVENTION AND THE RELATED ART]

[Field of the Invention]

The present invention relates to a polymer electrolyte for a lithium sulfur battery and a lithium-sulfur battery comprising the same, and more particularly, to a polymer electrolyte for a lithium sulfur battery that can provide batteries exhibiting good cycle life characteristics, and a lithium-sulfur battery comprising the same.

[BACKGROUND OF THE INVENTION]

The development of portable electronic devices has led to a corresponding increase in the demand for secondary batteries that both weigh less and have a higher capacity. To satisfy these demands, the most promising approach is a lithium-sulfur battery with a positive electrode made of sulfur-based compounds.

Lithium-sulfur batteries use sulfur-based compounds with sulfur-sulfur bonds as a positive active material, and alkali metal such as lithium metal or a carbon-based compound which can reversibly intercalate or deintercalate metal ions, such as lithium ions. Upon discharging (i.e., electrochemical reduction), the sulfur-sulfur bonds are cleaved, resulting in a decrease in the oxidation number of sulfur (S), and upon recharging (i.e., electrochemical oxidation), the sulfur-sulfur bonds are

re-formed, resulting in an increase in the oxidation number of the S so that the electrical energy is stored in the battery as chemical energy during charging and is converted back to electrical energy during discharging.

With respect to specific density, the lithium-sulfur battery is the most attractive among the currently developing batteries since lithium has a specific capacity of 3,830 mAh/g, and sulfur has a specific capacity of 1,675 mAh/g. Further, the sulfur-based compounds are less costly than other materials, and they are environmentally friendly.

However, employing a positive electrode based on elemental sulfur in an alkali metal-sulfur battery system has been considered problematic. Although theoretically the reduction of sulfur to an alkali metal-sulfide confers a large specific energy, sulfur is known to be an excellent insulator, and problems using it for an electrode have been noted, and such problems include a very low percentage of utilization and a low cycle life characteristic as a result of the sulfur and lithium sulfide (Li_2S) dissolved and diffused from the positive electrode.

Furthermore, the high reactivity of lithium metal negative active materials makes them undesirably react with electrolytes, and the reaction generates dendrites of lithium metal, thereby deteriorating cycle life characteristics.

It is expected that the reaction between the lithium metal and the electrolyte may be decreased in polymer electrolyte batteries than liquid-type electrolyte batteries, but the polymer electrolyte cannot be applied to lithium sulfur batteries. A general electrolyte is disclosed in U.S. Patent No. 6,329,103, in which a polymer electrolyte with polymerizable alkylene oxide polymer is taught, and in U.S. Patent No. 5,925,283, in which a halogen-substituted carbonic ester (non-cyclic carbonic ester) gel polymer is taught. However, these investigations are only applied to only lithium ion batteries, but cannot be applied to lithium sulfur batteries.

[SUMMARY OF THE INVENTION]

It is an object of the present invention to provide a polymer electrolyte for a lithium sulfur battery, which can effectively protect lithium metal.

It is another object to provide a polymer electrolyte for a lithium sulfur battery, which can provide batteries exhibiting good cycle life characteristics.

It is still another object to provide a lithium sulfur battery comprising the electrolyte.

[DETAILED DESCRIPTION OF THE INVENTION]

In one embodiment, the invention is directed to a polymer electrolyte for a lithium sulfur battery including a monomer including methacrylate groups; a C₆ to C₄₀ peroxide; and an electrolytic solution including an organic solvent; and a lithium salt.

The present invention also provides a lithium sulfur battery including the polymer electrolyte, a positive electrode including at least one positive active material selected from elemental sulfur, sulfur-based compounds, and mixtures thereof, and a negative electrode including a negative active material selected from materials that are capable of reversibly intercalating or deintercalating lithium ions, materials that react with lithium ions to prepare a lithium-included compound, lithium metals, and lithium alloys.

The present invention will be illustrated in more detail.

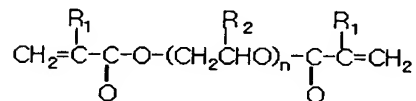
The present invention is directed to a polymer electrolyte that does not react with lithium metal. Thus, the polymer electrolyte does not cause deterioration of the cycle life characteristic associated with lithium dendrites by the reaction between a conventional electrolytic solution and lithium metal. Such a polymer electrolyte may be a gel polymer electrolyte, or alternatively a gelled solution-included polymer electrolyte which is polymerized to form a gel at about 75°C in the battery.

The polymer electrolyte includes a methacrylate-included monomer and a C₆ to C₄₀ peroxide, and electrolytic solution including an organic solvents, and a lithium salt. In the application, the organic solvent and a lithium salt are referred to as "electrolytic solution".

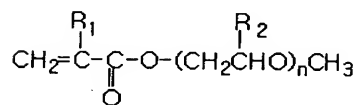
The methacrylate-included monomer has at least one carbon-carbon double bond at a terminal end, and the examples include multifunctional acrylates, poly(ethyleneglycol) dimethacrylate, poly(ethyleneglycol) diacrylate, poly(ethyleneglycol) divinylether ethylene glycol dimethacrylate, ethyleneglycol diacrylate, ethyleneglycol divinyl ether hexanediol diacrylate, tripropyleneglycol diacrylate, tetraethyleneglycol monoacrylate, caprolactone acrylate, and mixtures

thereof. Preferred are multifunctional acrylates and poly(ethyleneglycol) dimethacrylate, and most preferred is a multifunctional acrylate. The term "multifunctional acrylate" indicates poly(ester)(metha)(acrylate) in which hydroxide groups in (polyester)polyol with at least three hydroxides (-OH) are partially or totally substituted with (metha)acrylic ester, and un-substituted hydroxide groups are substituted with groups having no radical reactivity. Examples of suitable multifunctional acrylates are monomers represented by formulas 1 and 2:

Formula 1



Formula 2



where R_1 is H or a C_1 to C_6 alkyl group;

n is an integer ranging from 1 to 100,000; and

R_2 is H or a C_1 to C_6 alkyl group.

The mixing weight ratio of the electrolytic solution and the monomer is preferably more than 10 and 200 or less : 1, more preferably 40 to 150 : 1, and most preferably 60 to 120 : 1.

An amount of 10 times or less of the electrolytic solution to the monomer causes activation of a subsequent polymerization and forms a rigid solid electrolyte. The polymer electrolytes used in lithium sulfur batteries preferably have substantially intermediate physical properties between liquid and solid and more preferably properties closer to liquid rather than solid. An amount of more than 200 times the amount of electrolytic solution causes it to be squeezed from a polymer matrix.

The electrolyte includes an electrolytic salt and an organic solvent.

The organic solvent may be a sole solvent or a mixed organic solvent with at least two components. The mixed organic solvent includes at least two groups selected from weak polar solvent groups, strong polar solvent groups, and lithium protection groups, and some electrolytes include at least one or more solvents selected from the same group.

The term "weak polar solvent", as used herein, is defined as a solvent that is capable of dissolving elemental sulfur and that has a dielectric coefficient of less than 15, and the weak polar solvent may be selected from aryl compounds, bicyclic ether, and acyclic carbonate compounds; the term "strong polar solvent", as used herein, is defined as a solvent that is capable of dissolving lithium polysulfide and that has a dielectric coefficient of more than 15, and the strong polar solvent may be selected from bicyclic carbonate compounds, sulfoxide compounds, lactone compounds, ketone compounds, ester compounds, sulfate compounds and sulfite compounds; and the term "lithium protection solvent", as used herein, is defined as a solvent that forms a good protective layer, i.e. a stable solid-electrolyte interface (SEI) layer, on a lithium surface, and which shows a cyclic efficiency of at least 50%, and the lithium protection solvent may be selected from saturated ether compounds, unsaturated ether compounds, and heterocyclic compounds including N, O, and/or S.

Examples of the weak polar solvents include xylene, dimethoxyethane, 2-methyltetrahydrofuran, diethyl carbonate, dimethyl carbonate, toluene, dimethyl ether, diethyl ether, diglym, and tetraglyme.

Examples of the strong polar solvents include hexamethyl phosphoric triamide, γ -butyrolactone, acetonitrile, ethylene carbonate, propylene carbonate, N-methyl pyrrolidone, 3-methyl-2-oxazolidone, dimethyl formamide, sulfolane, dimethyl acetamide, dimethyl sulfoxide, dimethyl sulfate, ethylene glycol diacetate, dimethyl sulfite, and ethylene glycol sulfite.

Examples of the lithium protection solvents include tetrahydrofuran, 1,3-dioxolane, 3,5-dimethylisoxazole, 2,5-dimethyl furane, furane, 2-methyl furane, 1,4-oxane, and 4-methyldioxolane.

Examples of electrolyte salts which are optional for the battery of this invention include lithium trifluoromethane sulfonamide, lithium triflate or mixtures thereof. The concentration of the lithium salt is preferably 0.6 to 2.0M, and more

preferably 0.7 to 1.6M. If the concentration of the lithium salt is less than 0.6M, the conductivity of the electrolyte decreases, thereby deteriorating battery performance. If the concentration of the lithium salt is more than 2.0M, the viscosity of the electrolyte increases, thereby deteriorating movement of lithium ions.

In the present invention, by obtaining poly(ester)(metha)(acrylate) in which hydroxide groups in (polyester)polyol with at least three hydroxides (-OH) are partially or totally substituted with (metha)acrylic ester, and un-substituted hydroxide groups are substituted with groups having no radical reactivity, all acrylate groups in the poly(ester)(metha)acrylate monomer of the present invention participate in the polymerization, so that the poly(ester)(metha)acrylate monomer of the present invention has no shortcomings such as inferior low-temperature and cycle life characteristics, such as are associated with a non participation acrylate group.

The polyester polyol with at least three hydroxide groups may be obtained from general preparations, e.g. condensation polymerization of hydroxyl carbonic acid, open polymerization of lactone, or condensation polymerization of glycol and dicarbonic acid, or alternatively from markets. Examples of the polyester polyol with at least three hydroxide groups include trialkylols such as trimethylol, triethylol, and tripropylol; glycerols; and erythritols such as pentaerythritol and dipentaerythritol.

The hydroxide groups in the polyester polyol are partially or totally substituted with (metha)acrylic ester, and un-substituted hydroxide groups are substituted with a group having no radical reactivity, thereby producing poly(ester)(metha)acrylate or polymers thereof.

The substitution procedure may be performed under a condition of general esterification: a condensation of polyesterpolyol and (metha)acrylic halide in the presence of basic catalysts, or a condensation of polyesterpolyol and (metha)acrylic acid in the presence of acidic catalysts.

The condensation in the presence of basic catalysts will be illustrated below.

The (metha)acrylic acid halide may be acrylic chloride or (metha)acrylic chloride, and the amount of the (metha)acrylic acid halide is suitably 0.5 to 5 equivalents based on 1 M of a hydroxide group in polyesterpolyol.

The basic catalyst may be an organic base such as triethylamine, pyridine, dimethylaminopyridine, or diazabicycloundecene, or an inorganic base such as lithium carbonate, sodium carbonate, potassium carbonate, lithium hydroxide, sodium hydroxide, or potassium hydroxide. The amount of the basic catalyst is preferably 1.0 to 5.0 equivalents based on the amount of (metha)acrylic halide.

The reaction may be performed in the presence or absence of a solvent. Useful solvents include halogenated hydrocarbons such as dichloroethane and chloroform; aromatic hydrocarbons such as benzene, toluene, and xylene; saturated hydrocarbons such as hexane, heptane, decane and cyclohexane; and ethers such as diethylether, diisopropylether, and tetrahydrofuran.

The reaction may be performed at -20 to 100°C, and preferably -5 to 50°C.

The condensation of polyesterpolyol and (metha)acrylic acid, the amount of (metha)acrylic acid is preferably 0.1 to 10M based on 1M of a hydroxide group in polyesterpolyol. The acidic catalyst may be sulfuric acid, methane sulfonic acid, p-toluene sulfonic acid, hydrochloric acid, phosphoric acid, tungsten phosphate, or molybdenum phosphate. The amount of the acidic catalyst is preferably 0.01 to 10 wt% to polyesterpolyol.

The reaction is performed in an inert solvent, such as an aromatic hydrocarbon, e.g., benzene, toluene, or xylene; or a saturated hydrocarbon, e.g., hexane, heptane, decane or cyclohexane, and the produced water is preferably removed by an azeotropic reaction. The amount of the solvent is 0.1 to 10 parts by weight to polyesterpolyol. The reaction is performed at 50 to 200°C, and preferably 70 to 150°C.

According to the aforementioned procedure, hydroxide groups in the polyol are partially or totally substituted with (metha)acrylic ester. The substituted (metha)acrylic ester is preferably $-\text{OC}(=\text{O})(\text{CH}_2)_n\text{OC}(=\text{O})\text{CH}=\text{CH}_2$ or $-\text{OC}(\text{CH}_2)_nC(\text{CH}_3)=\text{CH}_2$, where n is an integer from 1 to 20.

Un-substituted hydroxide groups are substituted with groups having no radical reactivity.

The groups having no radical reactivity may be selected from C_1 to C_{20} aliphatic hydrocarbons, C_6 to C_{20} aromatic hydrocarbons, C_1 to C_{20} ethers, and

preferably $\text{OC(=O)(CH}_2)_2\text{CH}_3$, $-\text{O(C=O)Ar}$ where Ar is an unsubstituted or substituted aromatic hydrocarbon, $\text{OC(=O)(CH}_2)_n\text{O(CH}_2)_n\text{(CH}_3\text{)}$, where n is an integer from 1 to 20, $-\text{O(C=O)(CH}_2)_n\text{OC(=O)(CH}_2)_n\text{CH}_3$, where n is an integer from 1 to 20, and $-\text{O(C=O)CH=CH}_2$.

One of the procedures includes esterification of unreacted hydroxide groups using the radical unreactivity groups corresponding to the hydroxide groups. The radical unreactivity groups may be carbonyl acid or a halogen compound having a C_1 to C_{20} aliphatic hydrocarbon; or a carbonyl-based or halogen compound having a C_6 to C_{20} aromatic hydrocarbon, a C_1 to C_{20} ether, or a C_1 to C_{20} ester. An example thereof is butyl carbonic acid.

A modified polyester polyol may be used in the esterification and the modified polyester polyol is obtained from the ring-open polymerization of polyester polyol with lactones, and it has a modified structure. The modified polyester polyol renders control of a length of hydroxide groups which act as reactive groups in the molecular structure so that it effectively controls the physical properties of the electrolyte. The lactone may be ϵ -caprolactone or γ -caprolactone. The amount of the lactones depends on the total hydroxide groups of the polyesterpolyol. Thus, it is not necessary to limit the amount of the lactones, but according to solubility and size of molecules of the lactone-substituted modified polyester polyol, the amount of the lactones is 1000 mole% or less of the total hydroxide groups of the polyesterpolyol, and preferably 0.01 to 10M : 1M of the hydroxide groups of the polyol.

The catalyst to activate the ring-open polymerization may be selected from organic titanium-based compounds, organic tin-based compounds, and metal salts of an organic carbonic acid. An example of the organic titanium-based compound is tetrapropyltitanate.

The amount of the catalyst is preferably 0.001 to 1 parts by weight per 100 parts by weight of the lactones.

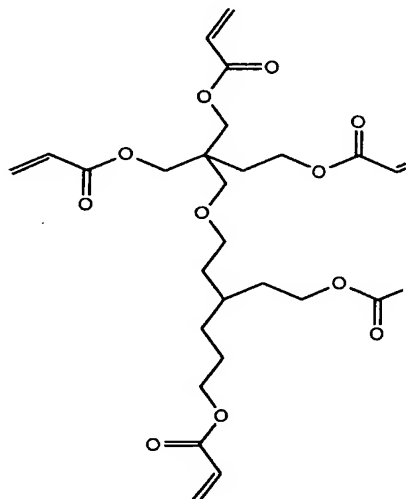
If a modified polyesterpolyol is used, the modified polyesterpolyol, acrylic acid or derivatives thereof, and the compound having a radical unreactivity group, are simultaneously mixed to cause esterification. The mole ratios between the acrylic acid or derivatives thereof, the modified polyesterpolyol, and the compound

allows the determination of a ratio between a substitution with (metha)acrylic ester and a substitution with a radical unreactivity group.

According to the aforementioned procedure, poly(ester)(metha)acrylate or a polymer thereof is prepared.

A preferred monomer is represented by Formula 3.

Formula 3



The mole ratio of (metha)acrylic ester and the radical unreactivity group is preferably 1 : 0.01 to 1 : 100. If the mole ratio is less than 1 : 0.01, the degree of crosslinkage increases to decrease ionic conductivity. If the mole ratio is more than 1 : 100, it does not activate a crosslink so it forms no polymer.

The polymer electrolyte includes a C₆ to C₄₀ peroxide. The peroxide acts to initiate polymerization of a polyester (metha)acrylate polymer, and has a -C(=O)-O-O-C(=O)-polar (hydrophilic) portion and a C₆ to C₄₀ aliphatic or aromatic hydrocarbon nonpolar (hydrophobic) portion.

The C₆ to C₄₀ peroxide generates CO₂ with good affinity with an electrolyte to improve initial charge and discharge efficiency of the battery, compared with an azobenzen-based initiator such as 2,2'-azoisobutyronitrile, which generates an inert gas, N₂, with no solubility to the electrolyte.

The initial charge and discharge efficiency of the lithium sulfur battery depends on a thin layer on the electrode, especially on the negative electrode. The

morphology of the thin layer affects the battery performance, and evenness of the thin layer renders good initial charge and discharge efficiency, and unevenness (extraction of lithium) causes inferior initial charge and discharge efficiency.

Examples of the C₆ to C₄₀ peroxide include isobutyl peroxide, lauroyl peroxide, benzoyl peroxide, m-toluoyl peroxide, t-butyl peroxy-2-ethyl hexanoate, t-butyl peroxybiphenylate, t-butyloxynodecanate, diisopropyl peroxy dicarbonate, diethoxy peroxy dicarbonate, bis-(4-t-butylcyclohexyl)peroxy dicarbonate, dimethoxy isopropyl peroxy dicarbonate, dicyclohexylperoxy dicarbonate, 3,3,5-trimethylhexanoyl peroxide, and mixtures thereof. Preferred are lauroyl peroxide and benzoyl peroxide.

The amount of peroxide is preferably 0.3 to 5 parts by weight based on 100 parts by weight of poly(ester)(metha)acrylate. If the amount of initiator is less than 0.3 parts by weight, it is difficult to polymerize, and if it is more than 5 parts by weight, too large a polymer is formed, which has deteriorated mechanical properties.

The poly(ester)(metha)acrylate preferably has a weight-average molecular weight of 300 to 100,000.

A method of fabricating a lithium sulfur battery using the polymer electrolyte will be described in more detail.

A monomer with a methacrylate group, a C₆ to C₄₀ peroxide, and an electrolyte are mixed to prepare a composition for preparing a polymer electrolyte.

Using the composition, a film-type polymer electrolyte is prepared, and alternatively, the composition is injected into a battery case and is polymerized in the battery. The film-type polymer electrolyte preferably has a thickness of 5 to 90 μm to provide good ionic conductivity.

The film-type polymer electrolyte is prepared by coating the composition on a substrate and polymerizing it by heat-treating or with UV radiation followed by separation of the resulting material from the substrate. The heat-treatment temperature depends on the half life of an initiator of the radical reaction, and it is suitably 40°C to 110°C, and preferably 60°C to 85°C. If the heat-treatment is performed at too low a temperature, the amount of the remaining unreacted monomer increases or the reaction time is long, causing an increase in cost. If the heat-treatment is performed at too high a temperature, excess lithium salt is

decomposed. The film-type polymer electrolyte additionally acts as a separator, and thus an additional separator is not required.

For polymerization in the battery, an electrode element is inserted into a battery case and the composition for preparing a polymer is injected into the case to fabricate a battery, and the electrode element includes a positive electrode, a negative electrode, and a separator interposed between the positive electrode and the negative electrode. The battery is allowed to stand at 70°C to 80°C for 2 to 6 hours. During this time, polymerization occurs to form a polymer electrolyte. The separator may be a polyethylene separator, a polypropylene separator, a polyethylene/polypropylene two-layer separator, a polyethylene/polypropylene/polyethylene three-layer separator, a polypropylene/polyethylene/polypropylene three-layer separator, or other suitable type of separator.

The positive active material includes elemental sulfur (S_8), a sulfur-based compound, or a mixture thereof. The sulfur-based compound may be selected from Li_2S_n ($n \geq 1$), an organic-sulfur compound, or a carbon-sulfur polymer $((C_2S_x)_n$; $x = 2.5$ to 50, $n \geq 2$). The negative active material includes lithium metal or a lithium alloy of lithium/aluminum.

The following examples illustrate the present invention in further detail, but it is understood that the present invention is not limited by these examples.

* Synthesis of Electrolyte

Comparative Synthesis Examples 1 to 8

Poly(ethylene glycol) dimethacrylate (PEGDMA) with an average molecular weight of 330 was added to a 1M solution of $LiN(SO_2CF_3)_2$ in dimethoxyethane/1,3-dioxolane (80/20 volume ratio) and shaken for 10 minutes. A trace of azobisisobutyronitrile (AIBN) was added to the resulting material and it was heated at 75°C for 4 hours to gel. The physical properties of the obtained electrolyte are presented in the following Table 1.

Table 1

	Component amount (g)			Physical properties
	Electrolyte	PEGDMA	AIBN	
Comparative Synthesis Example 1	30	1	0.01	No gelation and increase in viscosity
Comparative Synthesis Example 2	25	1	0.01	No gelation and increase in viscosity
Comparative Synthesis Example 3	20	1	0.01	No gelation and increase in viscosity
Comparative Synthesis Example 4	15	1	0.01	No gelation and increase in viscosity
Comparative Synthesis Example 5	12.5	1	0.01	Gelation
Comparative Synthesis Example 6	10	1	0.01	Gelation
Comparative Synthesis Example 7	7.5	1	0.01	Gelation
Comparative Synthesis Example 8	5	1	0.01	Gelation

As shown in Table 1, when the electrolyte is used in the amount equal to 1250% or less of the monomer, gelation occurs, but when the electrolyte is used in an amount equal to 1500% or more of the monomer, gelation does not occur.

The product according to Comparative Synthesis Example 6 was cast as a disk-type sample. The sample was attached to a stainless steel electrode, and ionic conductivity was measured at room temperature. The result was a good ionic conductivity of $2.0 \times 10^{-3}(\text{S/cm})$.

Synthesis Examples 1 to 7

A tetrapropyltitanate catalyst with an amount of 0.01 wt% of dipentaerythritol was added to a mixture of 1M dipentaerythritol, 2M ϵ -caprolactone, and toluene, and the resulting mixture was reacted at 50°C to synthesize dipentaerythritol in which a hydroxide group at a terminal end was substituted with ϵ -caprolactone. Thereafter, 4M of acrylic acid and 2M of butylcarbonic acid were reacted with 1M of the monomer to prepare a polyester hexacrylate-based compound (PEHA) in which four hydroxide groups (-OH) at the terminal of the monomer were substituted with

-OC(=O)(CH₂)₅OC(=O)CH₂=CH₂, and the remaining two hydroxide groups were substituted with -OC(=O)(CH₂)₃CH₃.

The polyester hexacrylate-based compound was added to a 1M solution of LiN(SO₂CF₃)₂ in dimethoxy ethane/1,3-dioxolane (80/20 volume ratio) and shaken for 10 minutes. A trace of AIBN was added to the resulting material and it was heated at 75°C for 4 hours to gel. The physical properties of the obtained product are shown in Table 2.

Table 2

	Component amount (g)			Physical properties
	Electrolyte	Polyester hexacrylate-based compound	AIBN	
Synthesis Example 1	60	1	0.01	Gelation and occurrence of slight leakage of the electrolyte
Synthesis Example 2	50	1	0.01	Gelation and occurrence of slight leakage of the electrolyte
Synthesis Example 3	40	1	0.01	Gelation and occurrence of slight leakage of the electrolyte
Synthesis Example 4	30	1	0.01	Gelation
Synthesis Example 5	20	1	0.01	Gelation
Synthesis Example 6	10	1	0.01	Gelation
Synthesis Example 7	5	1	0.01	Gelation

As shown in Table 2, when the amount of the electrolyte is equal to 3000% or less of the monomer, the gelation suitably occurs so that leakage of the electrolyte from the polymer matrix does not occur and 4000% or more causes the electrolyte to leak from the polymer matrix even though gelation occurs. That is, the small amount of the electrolyte was leaked from the polymer matrix.

The polymer matrices of Synthesis Examples 1 to 4 were cast into disk-type samples. Each of the samples was attached on a stainless steel electrode, and the ionic conductivity was measured at room temperature. The results showed good ionic conductivities of 2.5 X 10⁻³ (S/cm) in Synthesis Example 4 and 3.4 X 10⁻³ (S/cm) in Synthesis Example 5.

Comparative Synthesis Example 8: Use of polyethylene glycol divinyl ether (PEGDVE, molecular weight of 240)

The gelation tests were performed while the amount of the electrolytic solution was varied in amount equal to 500 to 3000% of the monomer, but no gelation occurred.

(Comparative Example 1)

67.5 wt% of elemental sulfur, 11.4 wt% of a SUPER-P conductive material, and 21.1 wt% of a polyethylene oxide binder were mixed in an acetonitrile solvent to prepare a positive active material slurry. The slurry was coated on a carbon-coated Al current collector. The coated current collector was pressed. The pressed current collector was dried at room temperature for 2 hours and re-dried at 50°C for at least 12 hours to produce a positive electrode.

Using the positive electrode and a lithium foil negative electrode, a lithium sulfur cell with a nominal capacity of 838mAh/g was fabricated. A 1M LiN(SO₂CF₃)₂ in dimethoxyethane/1,3-dioxolane (80/20 volume ratio) electrolyte was used.

Comparative Examples 2 to 7

Lithium sulfur cells were fabricated by the same procedure as in Comparative Example 1, except that a composition for preparing a polymer electrolyte was used. The composition was prepared by adding PEGDMA and AIBN to the electrolytic solution in the amounts as shown in Table 3. The electrolytic solution was 1M LiN(SO₂CF₃)₂ in dimethoxyethane (80/20 volume ratio).

The cells according to Comparative Examples 1 to 7 were charged and discharged under the following conditions, and capacity at various c-rate (characteristics) and cycle life characteristic were measured. The results are shown in Table 3. In Table 3, capacity retention is expressed as a percentage value referring to a capacity for the 20th cycle compared to a capacity for the first cycle in the cycle life test.

First: cycle: 0.1C discharge (cut-off: 1.5V)

Second cycle: 0.2C charge (cut-off: 120% of nominal capacity or 2.8V)

0.1C discharge (cut-off 1.5V)

Third cycle: 0.2C charge (cut-off: 120% of nominal capacity or 2.8V)

0.2C discharge (cut-off 1.5V)

Fourth cycle (1st in cycle life): 0.2C charge (cut-off: 120% of nominal capacity or 2.8V)

0.5C discharge (cut-off 1.5V)

Fifth or more cycles: the same as fourth cycle

Table 3

	Component ratio			Capacity at various C-rate (mAh/g)				Capacity at 0.5C for first cycle in the cycle life (mAh/g)	Capacity at 0.5C for 20 th cycle in the cycle life (mAh/g)	Capacity retention (%)
	Electrolyte	PEGDMA	AIBN	First cycle at 0.1C	0.1C	0.2C	0.5C			
Comparative Example 1	10	0	0	1522	797	793	804	804	877	109
Comparative Example 2	25	1	0.01	1058	843	709	562	562	473	84
Comparative Example 3	20	1	0.01	1097	835	670	517	517	453	88
Comparative Example 4	15	1	0.01	1099	839	647	500	500	403	81
Comparative Example 5	12	1	0.01	918	750	499	437	437	340	78
Comparative Example 6	10	1	0.01	1004	825	639	495	495	310	62
Comparative Example 7	8	1	0.01	827	820	610	462	462	278	60

As shown in Table 3, the cells according to Comparative Examples 2 to 7 with the composition exhibited inferior capacity and cycle life characteristics to that according to Comparative Example 1 with the electrolytic solution.

Comparative Examples 8 to 11

Lithium sulfur cells were fabricated by the same procedure as in Comparative Example 1, except that a composition for preparing a polymer electrolyte was used. The composition was prepared by adding PEGDMA and AIBN to an electrolytic solution as shown in Table 4. The electrolytic solution was 1M LiN(SO₂CF₃) in dimethoxyethane/1,3-dioxolane (80/20 volume ratio).

The cells according to Comparative Examples 1 to 4, 6, 8 to 11 were charged at 0.2C (cut-off: 120% of nominal capacity, or 2.8V) and discharged at 0.5C (cut-off 1.5V) 100 times. The lithium negative electrode was separated from the cell and exposed to the atmosphere to cause natural firing. The results are shown in Table 4.

Table 4

	Component ratio			Final condition	Firing result
	Electrolyte	PEGDMA	AIBN		
Comparative Example 8	30	1	0.01	No gelation and increases in viscosity	Two cells firing
Comparative Example 2	25	1	0.01	No gelation and increases in viscosity	One cell firing
Comparative Example 3	20	1	0.01	No gelation and increases in viscosity	No fire
Comparative Example 4	15	1	0.01	No gelation and increases in viscosity	No fire
Comparative Example 9	12.5	1	0.01	Gelation	No fire
Comparative Example 6	10	1	0.01	Gelation	No fire
Comparative Example 10	7.5	1	0.01	Gelation	No fire
Comparative Example 11	5	1	0.01	Gelation	No fire
Comparative Example 1	10	0	0	Electrolytic solution	Five cells firing

The cells according to Comparative Examples 2 to 4, 8 to 11 exhibited no firing, as opposed to that according to Comparative Example 1. This result is considered to come about because a polymer layer is formed on the lithium negative electrode, which prevents contact between a surface of lithium and moisture.

Examples 1 and 2

A lithium sulfur cell was fabricated by the same procedure as in Comparative Example 2 except that PEHA obtained from Synthesis Example 1 was used and the amount thereof was changed as shown in Table 5.

The charge and discharge of the cells according to Examples 1 and 2 were performed under the same conditions as above. The results are shown in Table 5, and for comparison, the result of Comparative Example 1 is also presented in Table 5.

Table 5

	Component ratio			Capacity at various C-rate (mAh/g)				Capacity at 0.5C for first cycle (mAh/g)	Capacity at 0.5C for 300th cycle (mAh/g)	Capacity retention (1) (%)	Capacity at 0.5C for 400th cycle (mAh/g)	Capacity retention (2) (%)
	Electrolyte	PEHA	AIBN	First cycle (0.1C)	0.1 C	0.2C	0.5 C					
Example 1	60	1	0.01	1347	796	762	708	708	398	56	358	51
Example 2	30	1	0.01	1264	724	651	563	563	-	-	-	-
Comparative Example 1	10	0	0	1522	797	793	804	804	313	39	-	-

As shown in Table 5, the cell according to Example 1 exhibited higher capacity retention and better cycle life characteristics than the cell of Comparative Example 1. The cell according to Example 1 with the larger amount of electrolyte exhibited higher capacity retention than that according to Example 2.

The cell according to Example 1 had a capacity corresponding to the cell of Comparative Example 1 at 0.1C and 0.2C, and a lower capacity than the cell of Comparative Example 1 at 0.5C. However, the cell according to Example 1 had good cycle life characteristics and capacity retention for 300th cycle of 56%, compared to a capacity retention for the cell of Comparative Example 1 of 39%. In particular, the cell according to Example 1 had a reduced capacity loss as the cycles were repeated and a 51% capacity retention for the 400th cycle, that is, a 5% capacity loss over the 100th cycle between the 300th and 400th cycles. These results are believed to come about because a corrosion of the lithium negative electrode is restrained, as determined by separating the negative electrode from a cell that was repeatedly charged and discharged.

The negative electrodes separated from the cells of Example 1 and Comparative Example 1 after completion of the cycle life test are shown in FIGs. 1 and 2, respectively. The negative electrode according to Example 1 was not substantially damaged and was clear (FIG. 1) after 400th cycle, whereas the negative electrode according to Comparative Example 1 (FIG. 2) was damaged with the formation of dendrites after 300th cycle.

Examples 3 to 6 and Reference Example 1

A lithium sulfur cell was fabricated by the same procedure as in Comparative Example 2, except that PEHA was used and the amount thereof was varied as shown in Table 6.

Table 6

	Component ratio			Final condition	Firing test result
	Electrolyte	Poly(ester)(metha)acrylate	AIBN		
Example 1	60	1	0.01	Gelation but slight leakage	1 cell firing
Example 3	50	1	0.01	Gelation but slight leakage	No firing
Example 4	40	1	0.01	Gelation but slight leakage	No firing
Example 5	30	1	0.01	Gelation	No firing
Example 6	20	1	0.01	Gelation	No firing
Example 2	10	1	0.01	Gelation	No firing
Reference Example 1	5	1	0.01	Gelation	No firing
Comparative Example 1	10	0	0	Electrolytic solution	5 cells firing

The cells according to Examples 1 to 6 had no natural firing, as opposed to Comparative Example 1. These results are believed to have occurred because a polymer film formed on the negative electrode prevented contact between the lithium and moisture.

The cycle life characteristics of the cells according to Example 1 and Comparative Example 1 are presented in Table 6. The charge was performed at 0.2C charge (cut-off: 120% of nominal capacity, or 2.8V) and at 0.5C discharge (cut-off 1.5V) for 300th cycle or more. The results are shown in Table 7 and FIG. 2.

Table 7

	Component ratio			Nominal capacity (mAh/g)	Capacity for first cycle (mAh/g)	Capacity for 300th cycle (mAh/g)	Capacity retention per nominal capacity (%)	Capacity for 400th cycle (mAh/g)	Capacity retention (%)
	Electrolyte	Poly(ester)(metha)acrylate	AIBN						
Example 1	60	1	0.01	838	1215	425	50.7	383.0	45.7
Comparative Example 1	10	0	0	838	1351	313	37.4		

The cell according to Example 1 had a slightly lower capacity and a better cycle life characteristic than that of Comparative Example 1.

These results are believed to have occurred because the fluidity of the electrolytic solution decreased to make movement of a polysulfide active material from the positive electrode to the negative electrode and the corrosion of lithium difficult. This is shown from the negative electrode after the repeated charge and discharge.

[The effect of the invention]

The polymer electrolyte of the present invention exhibits good cycle life characteristics.

[Claims]

WHAT IS CLAIMED IS:

1. A polymer electrolyte for a lithium sulfur battery comprising:
a monomer including a methacrylate group;
a C₆ to C₄₀ peroxide; and
an electrolytic solution comprising an organic solvent and a lithium salt.
2. The polymer electrolyte of claim 1, wherein the monomer is polyethyleneglycoldimethacrylate or poly(ester)(metha)acrylate in which hydroxide groups in (polyester)polyol are partially or totally substituted with (metha)acrylic ester, and un-substituted hydroxide groups are substituted with a group having no radical reactivity.
3. The polymer electrolyte of claim 2, wherein the monomer is poly(ester)(metha)acrylate in which hydroxide groups in (polyester)polyol are partially or totally substituted with (metha)acrylic ester and un-substituted hydroxide groups are substituted with a group having no radical reactivity.
4. The polymer electrolyte of claim 1, wherein the mixing weight ratio of the electrolytic solution to the monomer ranges from greater than 10:1 to 200:1.
5. The polymer electrolyte of claim 4, wherein the mixing weight ratio of the electrolytic solution to the monomer is 40 to 150 : 1.
6. The polymer electrolyte of claim 5, wherein the mixing weight ratio of the electrolytic solution to the monomer is 60 to 120 : 1.
7. The polymer electrolyte of claim 2, wherein the group having no radical reactivity is selected from the group consisting of C₁ to C₂₀ aliphatic hydrocarbon groups, C₅ to C₂₀ aromatic hydrocarbon groups, C₁ to C₂₀ ether groups, and C₁ to C₂₀ ester groups.
8. The polymer electrolyte of claim 7, wherein the group having no radical reactivity is selected from the group consisting of -OC(=O)(CH₂)₃CH₃, -OC(=O)Ar where Ar is an unsubstituted or substituted aromatic hydrocarbon group,

-OC(=O)(CH₂)_nO(CH₂)_nCH₃ where n is an integer from 1 to 20, -O(C=O)(CH₂)_nOC(=O)(CH₂)_nCH₃ where n is an integer from 1 to 20, and -O(C=O)CH=CH₂.

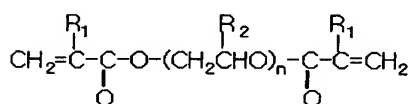
9. The polymer electrolyte of claim 2, wherein the monomer is a (metha)acrylic ester selected from -OC(=O)(CH₂)_nOC(=O)CH=CH₂ and -OC(=O)(CH₂)_nOC(=O)C(CH₃)=CH₂, wherein n is an integer of 1 to 20.

10. The polymer electrolyte of claim 1, wherein the monomer has at least one carbon-carbon double bond at a terminal end.

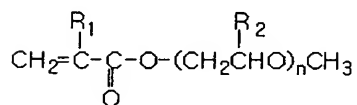
11. The polymer electrolyte of claim 1, wherein the monomer is selected from the group consisting of multifunctional acrylate, poly(ethyleneglycol) dimethacrylate, poly(ethyleneglycol) diacrylate, poly(ethyleneglycol) divinylether ethylene glycol dimethacrylate, ethylene glycol diacrylate, ethyleneglycol divinylether, hexanediol diacrylate, tripropyleneglycol diacrylate, tetraethyleneglycol monoacrylate, caprolactone acrylate and a mixture thereof, the multifunctional acrylate being poly(ester)(metha)acrylate in which hydroxide groups in (polyester)polyol are partially or totally substituted with (metha)acrylic ester and un-substituted hydroxide groups are substituted with a group having no radical reactivity.

12. The polymer electrolyte of claim 1, wherein the monomer is selected from compounds represented by the formulas 1 and 2:

Formula 1



Formula 2



where R₁ is H or a C₁ to C₆ alkyl group; n is an integer from 1 to 100,000; and R₂ is H or a C₁ to C₆ alkyl group.

13. The polymer electrolyte of claim 2, wherein the mixing mole ratio of the methacrylic ester and the group having no radical reactivity is 1 : 0.01 to 1 : 100.

14. The polymer electrolyte of claim 1, wherein the C₆ to C₄₀ peroxide is at least one selected from the group consisting of isobutyl peroxide, lauroyl peroxide, benzoyl peroxide, m-tolluoyl peroxide, t-butyl peroxy-2-ethyl hexanoate, t-butyl peroxy bibarate, t-butyloxynodecanate, diisopropyl peroxy dicarbonate, diethoxy peroxy dicarbonate, bis-(4-t-butylcyclohexyl)peroxy dicarbonate, dimethoxy isopropyl peroxy dicarbonate, dicyclo hexylperoxy dicarbonate, and 3,3,5-trimethylhexanoyl peroxide.

15. The polymer electrolyte of claim 1, wherein the initiator is present in an amount of 0.3 to 5 parts by weight based on 100 parts by weight of the polymer.

16. The polymer electrolyte of claim 2, wherein the polyester polyol is at least one selected from the group consisting of trialkylols, glycerols, and erythritols.

17. A lithium sulfur battery comprising:

a positive electrode comprising at least one positive active material selected from the group consisting of elemental sulfur, sulfur-based compounds, and mixtures thereof;

a negative electrode comprising a negative active material selected from the group consisting of materials that are capable of reversibly intercalating or deintercalating lithium ions, materials that react with lithium ions to prepare a lithium-included compound, lithium metals, and lithium alloys; and

a polymer electrolyte comprising a monomer including a methacrylate group, a C₆ to C₄₀ peroxide, and an electrolytic solution comprising an organic solvent and a lithium salt.

18. The lithium sulfur battery of claim 14, wherein the monomer is polyethyleneglycoldimethacrylate or poly(ester)(metha)acrylate in which hydroxide groups in (polyester)polyol are partially or totally substituted with (metha)acrylic ester, and un-substituted hydroxide groups are substituted with a group having no radical reactivity.

19. The lithium sulfur battery of claim 15, wherein the mixing weight ratio of the electrolytic solution to the monomer ranges from greater than 10:1 to 200:1.

20. The lithium sulfur battery of claim 19, wherein the mixing weight ratio of the electrolytic solution to the monomer is 40 to 150 : 1.

21. The lithium sulfur battery of claim 20, wherein the mixing weight ratio of the electrolytic solution to the monomer is 60 to 120 : 1.

22. The lithium sulfur battery of claim 21, wherein the group having no radical reactivity is selected from the group consisting of C₁ to C₂₀ aliphatic hydrocarbon groups, C₅ to C₂₀ aromatic hydrocarbon groups, C₁ to C₂₀ ether groups and C₁ to C₂₀ ester groups.

23. The lithium sulfur battery of claim 22, wherein the group having no radical reactivity is selected from the group consisting of -OC(=O)(CH₂)₃CH₃, -OC(=O)Ar where Ar is an unsubstituted or substituted aromatic hydrocarbon group, -OC(=O)(CH₂)_nO(CH₂)_nCH₃ where n is an integer of 1 to 20, -O(C=O)(CH₂)_nOC(=O)(CH₂)_nCH₃ where n is an integer of 1 to 20, and -O(C=O)CH=CH₂.

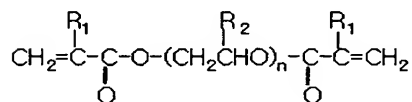
24. The lithium sulfur battery of claim 18, wherein the monomer is a (metha)acrylic ester selected from -OC(=O)(CH₂)_nOC(=O)CH=CH₂ and -OC(=O)(CH₂)_nOC(=O)C(CH₃)=CH₂, where n is an integer of 1 to 20.

25. The lithium sulfur battery of claim 18, wherein the monomer is selected from the group consisting of multifunctional acrylates, poly(ethyleneglycol) dimethacrylate, poly(ethyleneglycol) diacrylate, poly(ethyleneglycol) divinylether ethylene glycol dimethacrylate, ethylene glycol diacrylate, ethyleneglycol divinylether, hexanediol diacrylate, tripropyleneglycol diacrylate, tetraethyleneglycol monoacrylate, caprolactone acrylate and mixtures thereof, wherein the multifunctional acrylate is poly(ester)(metha)acrylate in which

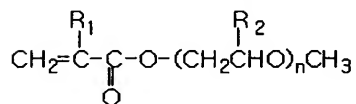
hydroxide groups in (polyester)polyol are partially or totally substituted with (metha)acrylic ester and un-substituted hydroxide groups are substituted with a group having no radical reactivity.

26. The lithium sulfur battery of claim 17, wherein the monomer is selected from compounds represented by the formulas 1 and 2:

Formula 1



Formula 2



where R_1 is H or a C_1 to C_6 alkyl group; n is an integer of 1 to 100,000; and R_2 is H or a C_1 to C_6 alkyl group.

27. The lithium sulfur battery of claim 24, wherein the mixing mole ratio of the methacrylic ester and the group having no radical reactivity is 1 : 0.01 to 1 : 100.

28. The lithium sulfur battery of claim 17, wherein the C_6 to C_{40} peroxide is at least one selected from the group consisting of isobutyl peroxide, lauroyl peroxide, benzoyl peroxide, m-tolluoyl peroxide, t-butyl peroxy-2-ethyl hexanoate, t-butyl peroxy bibarate, t-butyloxyneodecanate, diisopropyl peroxy dicarbonate, diethoxy peroxy dicarbonate, bis-(4-t-butylcyclohexyl)peroxy dicarbonate, dimethoxy isopropyl peroxy dicarbonate, dicyclo hexylperoxy dicarbonate, and 3,3,5-trimethylhexanoyl peroxide.

29. The lithium sulfur battery of claim 17, wherein the initiator is present in an amount of 0.3 to 5 parts by weight based on 100 parts by weight of the polymer.

30. The lithium sulfur battery of claim 18, wherein the polyester polyol is at least one selected from the group consisting of trialkylols, glycerols, and erythritols.

31. The lithium sulfur battery of claim 17, wherein the positive active material is selected from the group consisting of elemental sulfur, organic sulfur compounds selected from the group consisting of Li_2S_n , where $n \geq 1$, and Li_2S_n , where $n \geq 1$, dissolved in catholyte, and a carbon-sulfur polymer of the formula $(\text{C}_2\text{S}_x)_n$, where $x=2.5$ to 50 and $n \geq 2$.